Acta Mineralogica—Petrographica, Szeged, XXIII/2, 211—222, 1978

STRUCTURAL INFORMATIONS ON THE KEROGEN OF THE HUNGARIAN OIL SHALE

M. HETÉNYI and K. SIROKMÁN

INTRODUCTION

Geo-organic materials, among others the oil shales themselves, are extremely complex. Their chemical structure is recently hardly known and concerning the kerogen of the highly vexed oil shale of Green River (USA) only a working modell of ever changing character can be even established [YEN, 1976].

The basis of the method of structure research is the degradation of kerogen into smaller structural units. The most wide-spread degradation method is the oxidation and the most frequently but not solely used oxidation medium is the alkaline potassium permanganate. Based on the structural units formed during oxidation conclusions are tried to be drawn to the monomers forming the kerogen. In case of a given kerogen and according to the parameters of isolation and degradation procedure as well as to the applied analytical methods various results can be obtained, thus the conclusions of different authors are not always the same. Out of the forming compounds numerous ones can be produced by the oxidation of mineral components thus their removal from the kerogen is highly significant [DJURIĆIĆ *et al.* 1971]. The mode of the degradation procedure, *i.e.* it is carried out in one step or stepwise, leads to other conclusions. The temperature, the duration as well as the fact that the formed Mn(IV)-oxide is removed after each step or will be removed only after the completion of the whole degradation process, are only a few factors among those which may influence the composition of the product formed in this way.

The compounds produced during artificial decomposition are already rather complex, all the more so since these are not compounds but compound groups. Their analysis depends on the applied techniques and on the resolution capacity of the applied instruments. E.g. having analyzed the Green River kerogen after oxidation by means of gas-liquid chromatography significant quantity of straight-chain aliphatic structures was found which have been recently identified by means of proton-NMR-spectroscopy mostly as fused-ring cycloalkanes [YOUNG and YEN, 1977].

Though among the kerogens deriving from different localities and being of different ages and origin considerable differences may exist concerning their structures, the kerogens known so far and based on their oxidation behaviour can be assigned to several groups and those being assigned to the same group are nearly of the same structural built-up.

As to the working model mentioned above the Green River kerogen is a multipolymer, a non-uniform three-dimensional gel-network which is inhomogeneous due to its bio- and diagenesis. The multipolymer is built up by two kinds of monomers: by difunctional bridges and by multifunctional components. MURPHY

et al. [1971] who investigated also this kerogen, suggest it to consist of a central nucleus and of a periphery which is more advantageous from the point of view of degradation effects. According to DJURIĆIĆ [1971] the nucleus is built up by long polymethylene bridges.

The kerogen "tasmanite" is built up also by a nucleus and by the joining chains. The nucleus is of aromatic structure, its chains consist mostly of disordered, undersaturated hydrocarbon polymers [SIMOINET and BURLINGAME, 1973].

The kerogen of the Aleksinac oil shale of Yugoslavia is so highly heterogeneous that it consists of two structurally also different organic materials which has been proved both by chemical and by micropetrographic measurements. One part is humic, the other (being of greater amount) is more resistent and of bituminous character [VITOROVIĆ *et al.*, 1973]. This bituminous part consists of relatively long aliphatic chains which are bound by cross-bonds [STEFANOVIĆ *et al.*, 1959].

In this paper the partial results of the oxidation of kerogen of the Hungarian oil shale by potassium permanganate will be discussed. This oil shale was discovered by the co-workers of the Hungarian State Geological Institute [JÁMBOR Á. *et al.*, 1976]. The investigated sample derives from the borehole Put—7, in the environment of Pula. In the course of the degradation investigations of the kerogen we tried to assign it to any of the types mentioned above and to find similarities with other thoroughly investigated kerogens of oil shales, respectively. In favour to do this an oxidation and isolation method has been chosen which has been applied to the degradation of several different kerogens. Thus, the method of VITOROVIĆ *et al.* [1973] was followed. The organic acids formed during the analyses have been analyzed by means of infrared spectroscopy and gas-liquid chromatography.

EXPERIMENTAL

The sample of the Hungarian oil shale was placed at our disposal by the Hungarian State Geological Institute. The results of DTA and IR-investigations on Hungarian oil shale kerogen were reported by GY. GRASSELLY, M. BERTALAN and CS. SAJGÓ [1977].

The raw sample was ground and sieved down to mesh 100, than the soluble fraction was removed in Soxhlet extractor. The extraction was carried out by chloroform (Bit—A) resp. by the mixture of benzene: acetone: methanol (75:15:15; BAM). Having removed the soluble fraction the kerogen was separated from the mineral components by physical method, *i.e.* in aqueous solution of calcium chloride ($d=1.19$). The degree of purity of the kerogen was controlled by density and ash-content measurements. The characteristic features of the bitumen fractions as well of the kerogen are summarized in Table 1.

3.5 g kerogen (*i.e.* 3.25 g organic matter) was step-wise oxidized by alkaline potassium permanganate. The relationship between the time of oxidation and the oxidizing agent is shown in *Fig. 1.* In each step 1.25 g potassium permanganate was added in 100 ml potassium hydroxide of 1.6% and it was kept on water-bath of 60° C till the red colour of potassium permanganate disappeared and the brown colour of manganese dioxide occurred. The soluble products formed during oxidation were removed in order to prevent their further transformation. The solid part containing the unoxidized kerogen and the manganese dioxide was oxidized again in the second step under similar conditions described above. Since in the sixteenth step the potassium permanganate was not reduced already after 50 hours, oxidation was regarded to be complete. After the final oxidation step the surplus of po-

TABLE 1

Analytical data on organic matter of Hungarian oil shale

	Bitumen-A	Bitumen-BAM	Kerogen
		Original sample	
Quantity %	3.95	2.01	11.00
		Organic matter	
C %	68.90	74.80	73.60
H %	12.10	11.60	11,70
H/C atomic ratio	2.0	1.8	1.9
Ash %			8.0
Specific gravity g/cm³			1.1

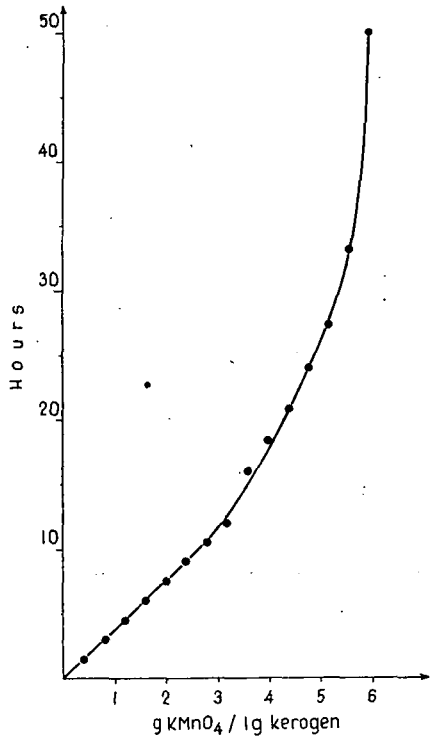

Fig. 1. Rate of oxidation, based on one gram of kerogen

tassium permanganate and the manganese dioxide were reduced by sulphur dioxide. The solid residue is about 5 per cent of the original organic matter.

In each steps the soluble products were treated separately *(Fig. 2)* following

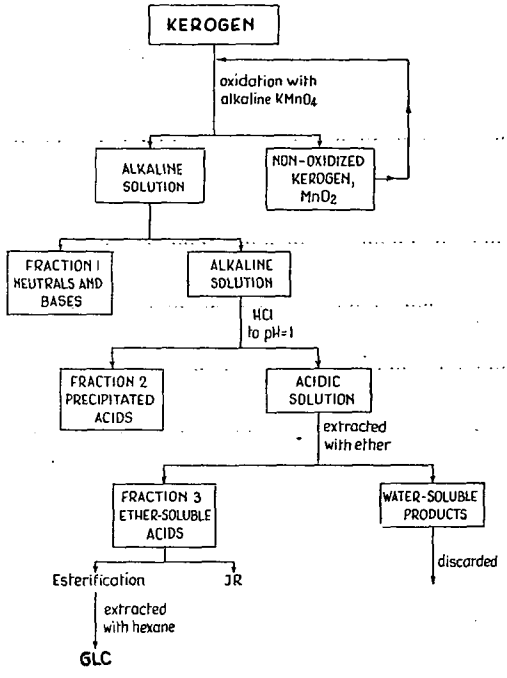

Fig. 2. Schematic outline of the experimental procedures

the method as below: the neutral and basic products were removed by ethereal extraction (1st fraction). The alkalic solution was acidifyed by hydrochloric acid to pH=1, the precipitated acids were removed by filtration (2nd fraction). The acid solution was etherifyed again collecting in the ethereal fraction the ether-soluble acids (3rd fraction). The total quantities of each fractions as well as the oxidation residue characterizing the kerogen of the Hungarian oil shale and the two checking samples are summarized in Table 2. The quantities of the fractions were determined in each steps and were plotted against the number of oxidation steps *(Fig. 3)*.

TABLE 2

Products and residue recovered by oxidation of different oil shales

Oil shales	Oxidation products Fraction 1 %	Fraction 2 %	Fraction 3 %	Residue %	Steps
Torbanite (Australia)	0.54	0.66	15.80	66.20	13
Aleksinac (Yugoslavia)	0.75	24.90	35.10	1.16	9
Oil shale (Hungary)	19.00	46.00	5.00	5.00	16
Green River (USA)	—	46.00	27.00	—	9

The ether-soluble acids were esterifyed by means of hydrochloric acidic methanol under carbon dioxide atmosphere during 120 minutes and treated at 80° C, then these were extracted by hexane and the hexane-soluble esters were analyzed by means of gas-liquid chromatograph (GLC).

Parameteres of the GLC: JEOL IGC—20K type; colonna: SP 23—40; temperature: 205° C.

The infrared spectroscopic records were made by UNICAM SP—200 equipment.

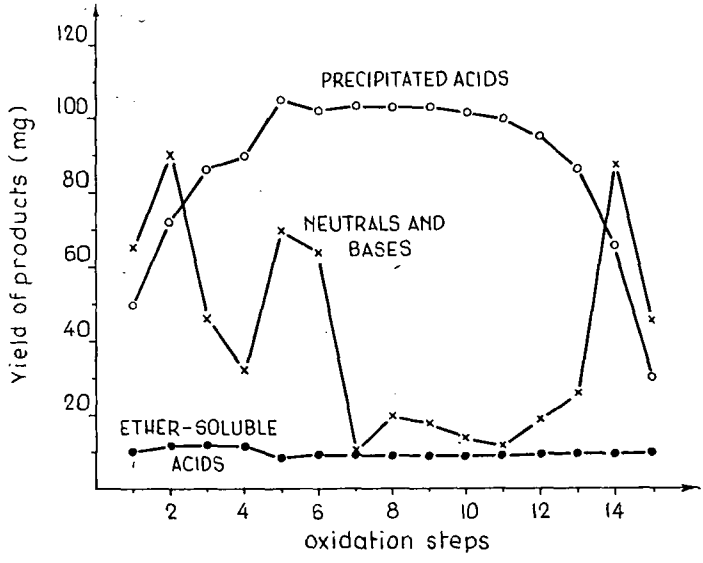

Fig. 3. The yield of oxidation products obtained from each step

RESULTS

The IR-records made from the oxidation products of kerogen as well as from the oxidation rest do not refer to the presence of aromatic acids. The IR-records made from the ether-soluble fractions of the steps 5 and 14 and from the non-oxidized residue are shown in *Fig. 4.* In Table 3 the common and most characteristic peaks of kerogens as well as their interpretation [SAXBY, 1976] are demonstrated. This Table shows also the evaluation of the most characteristic peaks of the IR-spectra of *Fig. 4,* as well as the checking coorongite, resp., its adequate wave number values, after CANE [1969]. The characteristic aromatic peaks (3000—3080 cm^{-1}, 1500—1520 cm^{-1}) are absent both in the spectra of the unoxidized residue and in those of the acids formed during oxidation similarly to those of coorongite. Though a smaller peak occurs at 740—850 cm^{-1} being attributed to aromatic rings by SAXBY but it is well-known that this range is characteristic not only of the compounds mentioned above, but of other inorganic and organic bond types. Thus, it cannot be accepted alone to prove the aromatic character.

As it is known, the oxidation method outlined above was adopted from coal chemistry to investigate the kerogens. During oxidation of coals under similar

TABLE 3

Infrared spectra of kerogens and ether-soluble acids derived from Hungarian oil shale kerogen

Kerogens (by SAXBY) cm^{-1}	Characteristic bands of infrared spectra of Hungarian oil shale kerogen			Coorongite (by CANE) cm^{-1}
	5. step cm^{-1}	14. step cm^{-1}	Residue cm^{-1}	
3310—3390 OH and NH bonds		3390—3500	3000—3850	3360
3000—3080 aromatic CH bonds	—	—	—	—
2900 aliphatic CH bonds	2900—2950	2900—2920	2920	2860—2950
1680—1745 C=0 bonds	1680—1710	1680—1710	1710—1720	1710—1735
1580—1650 C=C bonds H_2O deform. conj. C=0 bonds	1630		1620	1585
1500—1520 aromatic rings	—	—	—	—
1400—1460 aliphatic CH_2 and CH_3 groups	1410—1470	1410—1470	predominance of inorganic components	1460—1470
1370—1380 CH_3 and cyclic CH_2 groups	1380			1380
1090—1250 C—O bonds	1090—1250	1090—1250		1085—1140
890—980 C=C bonds	940			
740—850 condensed aromatic rings	790	—	790—810	840
720—725 aliphatic chains greater than C_4	720—730	720	725	725

conditions compounds of aromatic character are formed and the ratio of which increases with the progressing coalification. Consequently, the presence of aromatic acids among the oxidation products of kerogen relates to the fact that this organic matter contains also humic components while the absence of the aromatic acids

is characteristic rather of the kerogens of algal origin [CANE, 1976]. Accordingly, the kerogen investigated by us seems to be of pure algal origin. This statement is supported by the GLC measurements, too, which also did not relate to the presence of aromatic acids.

On the basis of the quantity of the unoxidizable residue the kerogens of the oil shales can be assigned to two groups. It is characteristic of the first group that

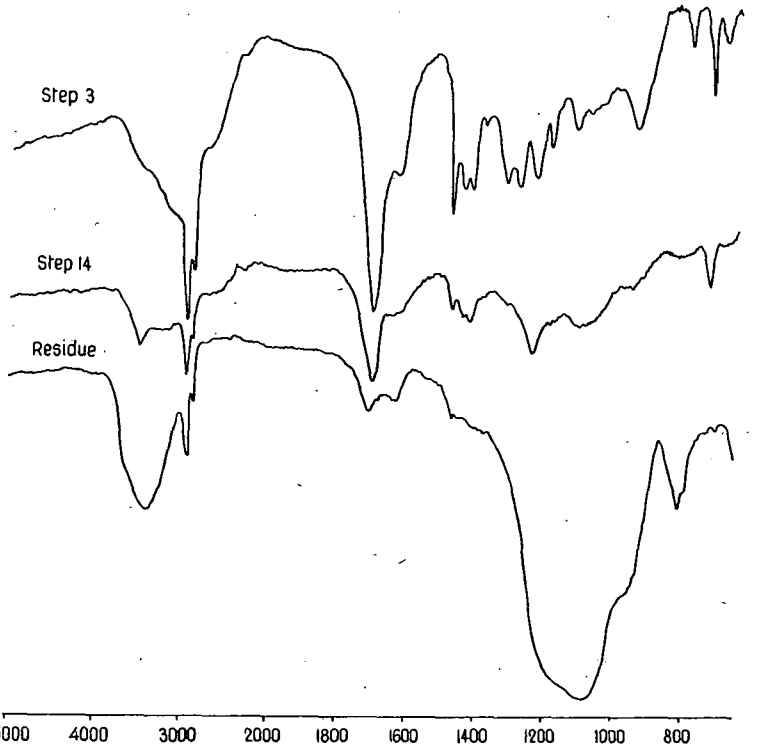

Fig. 4. IR-spectra of the unoxidized residue and ether-soluble acids obtained in the 5. and 14. oxidation steps

it can be nearly completely oxidized, e.g. the Green River oil shale (USA), kukersite kerogen (Soviet Union). The kerogens of the other group, e.g. the torbanite (Australia) are highly resistent to oxidation. According to our measurements the oxidation residue of the kerogen of the Hungarian oil shale amounts to about 5 per cent, *i.e.* it is assigned to the first group. According to CANE [1976] resistance is characteristic of the kerogens which derive from algal hydrocarbons, while the good efficiency of oxidation is characteristic of the kerogens derived from algal fatty acids. Thus, the kerogens of the Green River oil shale and those of the Hungarian oil shale might originate from algal fatty acids. The precursor of kerogen of the Hungarian oil shale is the alga *Botryococcus braunii* [JÁMBOR and SOLTI, 1976]. The lipid content of the freshwater algae amounts to about 60 to 70 per cent in the so-called "un-

favourable environment" being poorer in nitrogen salts [ABELSON, 1959]. The lipid content may consist of more than 80 per cent fatty acid. Thus, the fatty acid content of the alga might serve as the source of kerogen. Most of the fatty acids is unsaturated, consisting mainly of C_{16} and C_{18} and C_{14} and C_{20} are also found in relatively greater quantities. In the accumulation environment of the Hungarian oil shale the water level fluctuation of the small area, and parallel with this the extension and conditions of vegetation undergoing also frequent changes, have considerably influenced the oxygen production. The flourishing of vegetation increased the oxygen quantity, its extinction produced reductive environment [RAVASZ, 1976]. Immediately after the deposition following the destruction of the alga, *i.e.* when integrity of the cell wall ceased, the oxygen attacked the fatty acids and produced a highly polymerized kerogen as it has been evidenced by the results of the analyses performed by alkaline potassium permanganate oxidation. The high degree of polymerization is evidenced also by the fact that though kerogen is oxidizable nearly quantitatively, the oxidation is slow under the given experimental conditions. In *Fig. 1* the time of oxidation is plotted against the quantity of the oxidizing agent. When comparing its oxidation with that of the Yugoslavian Aleksinac oil shale [VITOROVIĆ *et al.*, 1973] — in which the duration continuously increases from 5 to 60 minutes in the first six steps, and this is more than 60 minutes already in the first step in case of the Hungarian oil shale; the oxidation time is the same in the first six steps and a slight increase between the seventh and twelwth and a sudden one after the twelwth step can be observed — it can be assumed that the Hungarian oil shale is probably of strongerly polymerized structure.

The elementary analysis and technological test of the oil shale lead to similar conclusions. The average oxygen content amounts to about 15 per cent which is a relatively high value. On the basis of the high bitumen content as compared to the soluble fraction and obtained by the FISHER-assay, the Hungarian oil shale has been qualified as an oil shale of progressed polymerization and of high kerogen content [ARATÓ and BELLA, 1976].

The fact that the quantity of the ether-soluble acids obtained during the oxidation is relatively small, relates also to high-grade polymerization. In Table 2 the products of oxidation of other kerogens performed in the same way, *i.e.* those of the Australian torbanite, of the Yugoslavian oil shale [DJURIĆIĆ *et al.* 1971], as well as the oxidation products of the Green River oil shale's kerogen obtained by different method but also with alkaline potassium permanganate [YOUNG and YEN, 1977] are summarized. Our measurement results concerning the oxidation of kerogen of the Hungarian oil shale are reported also in Table 2. When comparing the data it can be seen that during the oxidation of kerogen of the Hungarian oil shale relatively great amounts of solid acid are formed (fraction 2) while the third fraction is conspicuously small. According to VITOROVIĆ et al. [1973] the second and third fractions are the same concerning their chemical character. This was evidenced by the fact that having oxidized the second fraction by potassium permanganate, ether-soluble acids were obtained again. Following the previous procedure the solid acids deriving from the third step of oxidation of the Hungarian oil shale, ether-soluble acids were obtained by the repeated oxidation which similarly to the other products were analyzed as demonstrated in *Fig. 2.* The gaschromatograms of the ether-soluble acids formed in the 2nd, 6th and 12th steps are shown in *Fig. 5* which represent three phases of the oxidation process. Most of the products is a straight-chain aliphatic monocarbonic acid, between C_{14} and C_{24}. In harmony with the IR-spectra aromatic carbonic acids could not be detected. During similar investiga-

tions carried out in kerogens of other oil shales straight-chain aliphatic monocarbonic acids were also obtained in large quantities. E.g. having oxidized the Yugoslavian Aleksinac oil shale [VITOROVIĆ *et al.* 1973] monocarbonic acids of C_8—C_{26} were identified. On the basis of the gas chromatograms of the kerogen's oxidation products of the Green River oil shale, the oxidation products seemed to be mostly straight-chain aliphatic components [YOUNG and YEN, 1977]. The coorongite was degraded by potassium permanganate [CANE, 1969]. The coorongite represents a very early stage of the formation of algal kerogens and can be regarded as the peat-state during the coalification of algal shales. Among the acidic products mostly mono- and dicarbonic acids of C_{16}—C_{22} were identified.

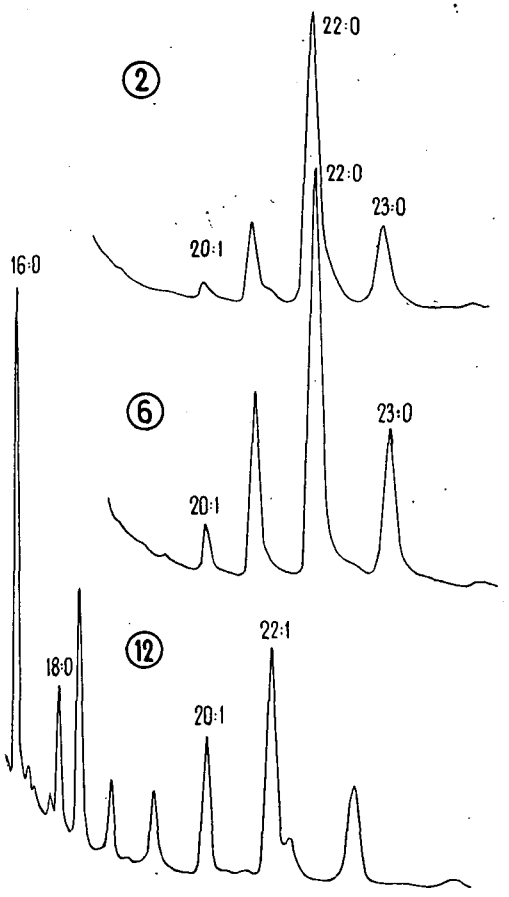

Fig. 5. The gas chromatogram of the ether-soluble acids obtained in the 2., 6. and 12. oxidation steps

Investigating the produced monocarbonic acids as a function of the oxidation time, in the first six steps (in which the oxidation time is shorter and is the same) the gas chromatograms seem to be the same. This is illustrated in *Figs. 5a* and *5b* were the gas chromatograms of the ether-soluble acids of the 2nd and 6th steps are

shown. Major part of the oxidation products is $C_{22:0}$, in smaller amounts $C_{23:0}$ and $C_{21:1}$ aliphatic monocarbonic acids are also found. (The mode of designation is as follows: $C_{N:M}$, where N denotes the atom-number of C, M is the number of double-bonds.)

From the 7th step the analytical results of the GLC analyses show some changes in addition to the increase of the oxidation time. Since from this step the gas chromatograms are roughly the same in all steps, only one of them will be presented *(Fig. 5c)*. When comparing this with the *Figs. 5a* and *5b* it is seen that in the second part of oxidation the composition of the ether-soluble acids is more variegated. Mostly $C_{16:0}$ and $C_{22:1}$ as well as $C_{20:1}$ and $C_{18:0}$ aliphatic monocarbonic acids were identified.

The further oxidation of the solid acids obtained in the 3rd step and investigating the ether-soluble acids by GLC mostly $C_{22:1}$ and $C_{20:0}$ aliphatic monocarbonic acids were identified. When comparing this result with the analysis of the ether-soluble acids obtained in the 3rd step, it is obvious that during repeated oxidation the oxidation products show a composition being rather similar to the original one.

Based on these results it seems to be probable that the kerogen of the Hungarian oil shale is highly polymerized and is a "macromolecule" built up by aliphatic hydrocarbons as evidenced by the GLC analyses.

SUMMARY

The Hungarian oil shale's kerogen was degraded into smaller and simpler compounds which are, however, in structural relation with the complex starting material.

The products relate to the structure of kerogen, the character of the products as well as the efficiency of degradation conclusions can be drawn concerning the precursor and possible source of the organic matter, further the type of the organic compounds.

Degradation was carried out by alkaline potassium permanganate which reacts with the carbon atom of functional groups or with the neighbouring one.

Oxidation was carried out step by step in favour to prevent the further oxidation of the products.

In the 16th step the duration of oxidation is more than 50 hours, thus the process was regarded to be completed, all the more so since in this stage only 5 per cent of the organic matter remained unoxidized.

Investigating the unoxidized and oxidized products compounds of aromatic character were not detected either by IR or by GLC method. This relates to the fact that the organic matter investigated is practically of algal origin and does not contain humic compounds. According to the classification of CANE [1976] it is assigned to "kerogen—A". On the basis of the efficiency of oxidation (which proved to be very good, *i.e.* unoxidized kerogen hardly remained) a finer subdivision was also made, thus the material is assigned to the type *A(i)*, *i.e.* it may derive mostly from algal fatty acids.

Taking into account that the precursor of the Hungarian oil shale is the alga *Botryococcus braunii*, its C_{16} and C_{18}, mostly unsaturated fatty acids were probably the source material of the kerogen.

The unsaturated fatty acids were highly polymerized just after the destruction of the algae and produced a complex "macromolecule". In addition to the elementary analysis of the oil shale (considerable oxygen content) and to the technological analyses (results of the FISHER-assay) the fact refers also to this fact that though it can be practically totally oxidized by alkaline potassium permanganate the single

oxidation steps, however, need much more time than, e.g. in case of the Yugoslavian oil shale oxidized in a similar way.

The distribution of the oxidation products among the three fractions supports also the high-grade polymerization. Relatively small amount of ether-soluble acids was formed though the chemical character of the solid acids being the major part of the degradation products, is rather similar to that of the ether-soluble acids. The similarity of the two fractions is evidenced by the fact that repeated oxidation on the solid acids resulted in ether-soluble acids again.

Analyzing the ether-soluble acids produced by oxidation by means of GLC considerable quantity of aliphatic monocarbonic acid was detected. Thus, their change was followed as a function of progressing oxidation. No conspicuous change was determined during the oxidation process, the aliphatic monocarbonic acids are C_{16} to C_{24}, they are saturated in general or contain at least one unsaturated bond. Some change can be observed from the 7th step; before this the major part of the products is $C_{22:0}$ and $C_{23:0}$, while in the second part of oxidation mostly $C_{16:0}$ and in smaller quantity $C_{18:0}$ aliphatic monocarbonic acids were identified in addition to the $C_{22:1}$ and $C_{20:1}$ ones.

ACKNOWLEDGEMENT

Authors express their thanks to DR. Á. JÁMBOR for providing the samples investigated and to DR. J. KONDA, Director of the Hungarian State Geological Institute for encouraging and assisting this research work.

REFERENCES

ABELSON, P. H. [1959]: Geochemistry of organic substances. — In: Researches in Geochemistry edited by P. H. Abelson. J. Wiley and Sons, Inc., Publishers. p. 79—104.

ARATÓ, K. and M. BELLA [1976]: Results of technological and chemical analyses of the oil shale of Pula and Gérce (Transdanubia, Hungary). — Annual Report of the Hungarian Geological Institute of 1974. p. 287—300.

CANE, R. F. [1969]: Coorongite and the genesis of oil shale. — Geochim. et Cosmochim. Acta *33*, p. 257—265.

CANE, R. F. [1976]: The origin and formation of oil shale. — In: Oil shale, edited by T. F. Yen an G. V. Chilingarian. Elsevier Scientific Publishing Company p. 27—61.

DJURIĆIĆ, M., R. C. MURPHY, D. VITOROVIĆ and K. BIEMANN [1971]: Organic acids obtained by alkaline permanganate oxidation of kerogen from the Green River (Colorado) shale. — Geochim. et Cosmochim. Acta *35*, p. 1201—1207.

DJURIĆIĆ M. V., D. VITOROVIĆ, B. D. ANDRESEN, H. S. HERTZ, R. C. MURPHY, G. PRETI and K. BIEMANN [1972]: Acids obtained by oxidation of kerogens of ancient sediments of different geographic origin. — Adv. in Org. Geochem., 1971 p. 305—321.

GRASSELLY, GY., M. BERTALAN and CS. SAJGÓ [1977]: Contributions to the knowledge of the Hungarian oil shale kerogen II. Result of preliminary DTA and IR-investigations on the kerogen of the oil shale occurrence at Pula. — Acta Miner. Petr., *XXIII/1*, p. 165—175.

JÁMBOR, Á. and SOLTI, G. [1975]: Geological conditions of the Upper Pannonian oil shale deposit recovered in the Balaton Highland and at Kemeneshát. — Acta Miner. Petr., *XXII/1* p. 9—28.

JÁMBOR, Á. and G. SOLTI [1976]: Geological conditions of the Upper Pannonian oil shale deposit recovered in the Balaton Highland and at Kemeneshát (Transdanubia, Hungary). — Annual Report of the Hungarian Geological Institute of 1974. p. 193—220.

RAVASZ, CS. [1976]: Petrographic examinations of oil shale at Pula and Gérce. — Annual Report of the Hungarian Geological Institute of 1974. p. 221—246.

SAXBY, J. D. [1976]: Chemical separation and characterization of kerogen from oil shale. — In: Oil shale, edited by T. F. Yen and G. V. Chilingarian. Elsevier Scientific Publishing Company. p. 103—121.

SIMONEIT, B. R. and A. L. BURLINGAME [1973]: Carboxylic acids derived from Tasmanian tasmanite by extractions and kerogen oxidations. — Geochim. et Cosmochim. Acta *37*, p. 595—610

YEN, T. F. [1976]: Structural aspects of organic components in oil shales. — In: Oil shale, edited by T. F. Yen and G. V. Chilingarian. Elsevier Scientific Publishing Company. p. 129—147.
YOUNG, D. K. and T. F. YEN [1977]: The nature of straight-chain aliphatic structures in Green River kerogen. — Geochim. et Cosmochim. Acta *41*, p. 1411—1418.
VITOROVIĆ, D., M. V. DJURIĆIĆ and B. ILIĆ [1973]: New structural information obtained by stepwise oxidation of kerogen from the Aleksinac (Yugoslavia) shale. — Advances in Organic Geochemistry 1971, p. 179—189.

Manuscript received, May 20, 1978

MISS DR. M. HETÉNYI
Institute of Mineralogy, Geochemistry
and Petrography
Attila József University
H-6701 Szeged, Pf. 428,
Hungary

MRS. KLÁRA SIROKMÁN
Institute of Biochemistry
Biological Research Center
Hungarian Academy of Sciences
H-6701 Szeged, P.O.B. 521,
Hungary